Qualitative Simultaneous Identification of Permanent and Hydrocarbon Gases by GC-TCD using Column Coupling Method

Oman Zuas*, Muhammad Rizky Mulyana

Gas Analysis Laboratory (GasAL), Metrology in Chemistry Research Group (MiCG), Research Centre for Metrology (RCM)-Indonesian Institute of Sciences (LIPI), Build. No. 456. Kawasan PUSPIPTEK Serpong 15314, Tangerang Selatan, Banten, Indonesia.

oman.zuas@lipi.go.id

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The potential application of the GC-TCD using column coupling method was investigated by means of comparison with the single column method for the identification of gas mixture containing 5 permanent and 6 hydrocarbon gases. The results indicate the useful of column coupling method, relative to the single column method. In addition, the flow rate of carrier gas and column temperature on the retention time of the target components have a noticeable effect. Application of the column coupling method for qualitative identification of the targeted components in natural gas samples indicate that the method can be used for routine work in the field of natural gas measurement, since the method has proven to be able to separate both hydrocarbon and permanent gas simultaneously. All the gas components that cannot be separated in the first column were well separated in the second column, which proved that column coupling method is superior to the single column separation.

Introduction

The gas chromatography (GC) was first invented in early 1900s [1]. Since then, the GC became a well-known as one of the most powerful technique in the area of chemical analysis and has been continually developed to increase its work efficiency. The efficiency of GC is often associated with the work to reduce the cost by using inexpensive carrier gases such as N_2 or H_2 which is economically advantageous [2, 3]. Although the use of inexpensive carrier gases is an example of good approach, an effort to improve column performance also remains concerned [4, 5].

In a GC experiment, the functional property of the columns (stationary phase) is considered as material for the separation process of eluted target component before the detection by the GC detector [6]. Upon detection by the detector, the target components can be qualitatively identified based on their retention time (t_R) [7].

As far as, the improvement of column performance has been extensively devoted in the area for achieving better separation and resolution by involving many technology advancement [4, 8-10]. In addition to improve the GC column performance for better separation and resolution, technology advancement for reducing the span of the GC measurement time has also been made. In this regards, method advancement of the GC column configuration system has been reported previously [11-13]. This column configuration system is known as column coupling method. Practically, the column coupling method consists of two columns having different stationary phase material was connected serially and configured by locating one column precedes the others or the reverse [12]. This method can also be classified as multidimensional gas chromatography, in which the sample was subjected to multiple separation processes (two in this case) coupled on-line. If the mentioned separation processes have different mechanisms and independent from each other, the orthogonality principle can then be fulfilled. An orthogonal system will result in an independent retention mechanism which, theoretically, will result in a more efficient compounds separation [14].

Application of column coupling method for the separation of a complex mixture is considered more favorable than the single column method (a GC system configured with one column). Each column in the column coupling configuration contains difference stationary phase material that allows such stationary phases to have different interactions with the target component, making possible for a simultaneous separation of different target components in a complex mixture based on their chemical properties [12, 15].

In this paper, experimental results from the qualitative simultaneous measurement of a gas mixture containing 11 target components of hydrocarbon and permanent gases by GC-TCD using a column coupling method are reported. The column coupling method was carried out by using two difference packed columns i.e., SP-1700 and MS-5 that were coupled in series and then installed on the GC-TCD system. The qualitative data from the column coupling method was compared to that of single column method. The effect of GC operating parameters (column temperature and flow rate of carrier gas) was also investigated. In addition, the application of the column coupling method was conducted for the qualitative identification of the target components in natural gas samples.

Experimental

Materials

Ultra high purity (> 99.99% purity) commercial gases including carbon dioxide (CO_2), hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon monoxide (CO), methane (CH_4),

ethane (C_2H_6), propane (C_3H_8), propylene (C_3H_6), iso-butane (iso-C_4H_{10}), and n-butane (n-C_4H_{10}) were used without any further purification.

A test mixture used in this study was prepared by transferring the necessary amount (~50-80 ml) of each gas into 1000 ml Tedlar® gas bag. Since the test mixture is subjected to a qualitative evaluation, exact concentration of all target components in the test mixture was not taken into account in this study.

Two other commercial grade natural gases were used as samples to evaluate the column coupling method for its application to identify gas components. The first commercial natural gas, coded as Sample-1, contains unknown components in C_3H_8 balance (Pertamina Gas, Indonesia) while the second, coded as Sample-2, mostly consist of C_3H_8 and C_4H_{10} along with other unknown minor components (MESA Specialty Gases and Equipment, USA).

Instrumentation

For the identification of all target components (component 1 through 11) in their mixture (Table 1), a GC instrumentation system (Agilent Model 6890 series, CA, USA) equipped with thermal conductivity detector (TCD) and stage dual-packed column configuration was used.

The column #1 (23% SP-1700 packed SS column, 3 feet x 1/8 inch o.d. x 2 mm, 80-100 mesh particle size, Supelco Sigma-Aldrich, USA) was connected in series with the column #2 (Molecular sieve 5A column, 9 feet x 1/8 inch o.d. x 2 mm, 80-100 mesh particle size, Restek, USA). Table 2 lists the operating conditions of the GC-TCD system. The carrier gas used was purified before entering the column using hydrocarbon filter (activated charcoal, Agilent Technology, USA).

Table 1. Target component

Gas type	Component
Permanent gases	CO_2, H_2, O_2, N_2, and CO
Hydrocarbon gases	CH_4, C_2H_6, C_3H_8, C_3H_6, iso- C_4H_{10}, and n- C_4H_{10},

Column Method Procedure

In this study, 11 target components in test mixture (Table 1) were not only separated using column coupling method using column #1 and #2 simultaneously (denoted as method-A+B), but also using single column method i.e., single column #1 (denoted as method-A) and single column #2 (denoted as method-B).

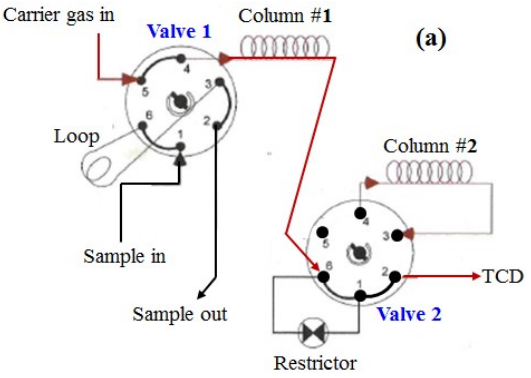
Table 2. Operating conditions of the GC-TCD under study

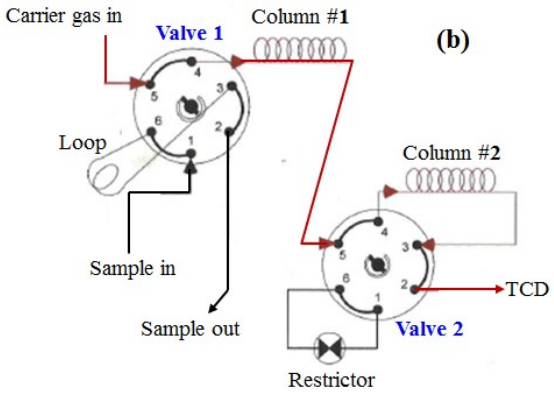
Parameter	Data
Injector temperature	100°C
Loop	2 ml
Oven temperature	40°C (isothermal)

Detector temperature	250°C
Carrier gas flow rate rate	20 ml/min
Make-up gas flow rate	7 ml/min
Signal source / data rate	5 Hz/0.04 min

The basic layout of each column method is configured as shown in Fig. 1a-c. Typically, the experiments were carried out as the below steps.

The first experiment was conducted by injecting the test mixture into GC-TCD and the target components were separated using method-A (Fig. 1a). Under this condition, the valve 2 was switched OFF at the first 2 min (Table 3). The carrier gas containing the test mixture passed through the SP-1700 column. All target components were eluted from SP-1700 column. The eluted target components from SP-1700 column were then detected by the TCD. Under this column configuration, no separation in MS-5A column was occurred.





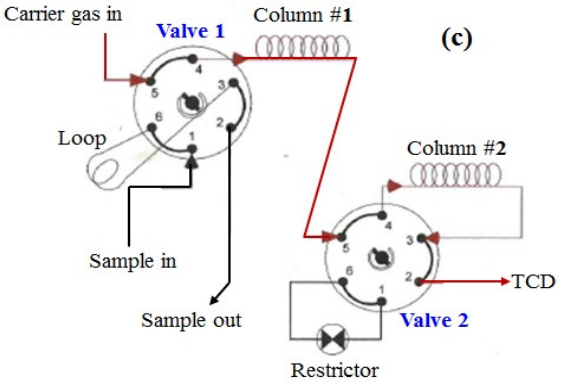


Figure 1. Basic of column configuration on: a) method-A, b) method-B, and c) method-A+B.

The second experiment was done by using method-B with a similar procedure to that of the first experiment, except column #2 (MS-5A column) was used instead of using column #1 (SP-1700 column) (Fig. 1b). In this method-B, the valve 2 was switched OFF at first 2 min (Table 3), the carrier gas (He) brought the test mixture to MS-5A column. Immediately, the target components in the test mixture were eluted from MS-5A column. The eluted target components from MS-5A column were then detected by the TCD, while no separation occurred in SP-1700 column (column #1).

Table 3. Valve status of the GC-TCD syatem

Method-A		Method-B		Method-A+B	
Time (min)	Valve 2 status	Time (min)	Valve 2 status	Time (min)	Valve 2 status
2	ON	2	OFF	2	ON
17	OFF	17	ON	8	OFF
-	-	-	-	17	OFF

The third experiment was performed by applying the column coupling method (method-A+B) (Fig. 1c). Under condition of the method-A+B, the test mixture was injected into the GC-TCD. Firstly, after the valve 2 was switched ON at the first 2 min (Table 3), the carrier gas (He) brought the test mixture into the SP-1700. The separation of the target component on SP-1700 column was occurred at 2 - 8 min (Table 3). After that, the valve 2 was immediately switched OFF at the retention time of 8 min (Table 3) and the target components were separated in MS-5A column (column #2). The separation of the target components in MS-5A column was occurred from 8-17 min (Table 3). All separated component eluted from both SP-1700 and MS-5A column were detected by the TCD. As a summary, the first experiment utilized the SP-1700 column for separation of the components; while the second experiment utilized MS-5A column instead. Finally, the third experiment combined both SP-1700 and MS-5A for simultaneous separation in one analysis runtime.

Analysis of Target Gas Components

Measurement of all target gas components in the test mixture were conducted by injecting a certain amount of test mixture into the column of the GC-TCD system under operating conditions as tabulated in Table 2. The GC-TCD chromatograms of the test mixture were evaluated by automated integration of the area under the resolved chromatogram profile using a software (OpenLAB CDS Chemstation version A.2.3.57.HP) installed on a personal computer (HP Pavilion Slimline 400 series). For the comparison of the aforementioned methods, the consecutive steps for the measurement of the test mixture were carried out as follows. Firstly, the test mixture was measured by the GC-TCD using the method-A. Secondly, the measurement was carried out using method-B. Finally, the test mixture was measured by method-A+B.

Effect of GC-TCD Operating Conditions

The effect of GC-TCD operating condition were studied by evaluating the effect of column temperature and carrier gas flow rate on the separation of the target components. In this case, the method-A+B was only used. Typically, the test mixture was injected into the GC-TCD under the same operating condition as shown in Table 2,

except the column temperature and carrier gas flow rate were varied. The variation of the oven temperature were 35 °C, 40 °C and 45°C and the carrier gas flow rate were 25 ml/min, 28 ml/min, and 31 ml/min.

Application of Column Coupling Method

The method-A+B (column coupling method) was evaluated for its application to identify gas components in two different commercial natural gas samples, coding with Sample-1 and Sample-2. Each natural gas sample was injected into GC-TCD under operating condition as shown in Table 2. Component identification in the gas sample was carried out by matching the identified component in natural gas sample with the component in the test mixture.

Results and discussion

Comparison between Single and Column Coupling Method

Increase the efficiency of the GC-TCD for a simultaneous measurement of permanent and hydrocarbon in term of shortening the span of measurement time was evaluated. Figure 2a-c presents the GC-TCD chromatogram profile of the target components in the test mixture separated on the column using three different methods (method-A, method-B, and method-A+B).

Figure 2a displays the chromatogram profile of the target component in test mixture separated in SP-1700 using method-A. As it can be seen from Fig. 2a that only six target components (component 1 through components 6) were resolved by SP-1700 column, while five other components (component 7 through components 11) remains unresolved. The ability of the SP-1700 (column #1) for resolving of components 1 through 6 is reasonable because the SP-1700 column is a typical of column for the separation of hydrocarbon components [16]. Besides, other components such CO_2 and air in the form of its composite (O_2+N_2) can also be resolved using the SP-1700 column [17].

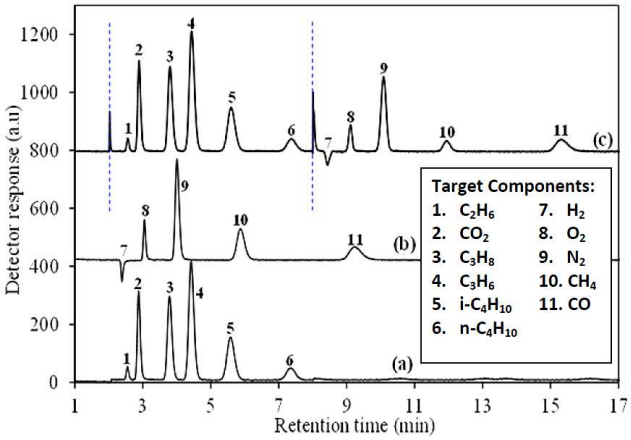


Figure 2. Chromatogram profile of the 11 target components separated using: a) SP-1700 column (method-A), b) MS-5A column (method-B), and c) column coupling method (method-A+B). The vertical blue dotted line indicates the time position of the switching valve.

Moreover, Figure 2b shows a chromatogram profile of the target components in the test mixture separated on MS-5A column (column #2). This MS-5A column contains a valuable material as a

stationery phase which is not only suitable for the separation of permanent gases such as H_2, CO_2, N_2, O_2, and CO, but also some light hydrocarbon components such as CH_4 and C_3H_8 [17-19]. From Fig. 2b, it can be observed that five target component (component 7 trough component 11) in the test mixture can be resolved on the MS-5A column and detected by the TCD.

Figure 2c presents a profile of chromatogram of the test mixture after simultaneously separation on both SP-1700 column (column #1) and MS-5 column (column #2) by using method-A+B with 17 min of the measurement time. From Fig. 2c, it can be seen that all target components (11 components) can be well resolved and identified by the TCD. In this column coupling method (Method-A+B), the six target components (component 1 through component 6) were resolved in SP-1700 (column #1), while other five target components (component 7 through components 11) were resolved on MS-5A column (column #2). Since the SP-1700 column was coupled to the MS-5A column in parallel position; thus, the profile of the chromatogram obtained (Fig. 2c) is found to be similar to that of chromatogram as a combination between the SP-1700 (Fig. 2a) and MS-5A column (Fig. 2b). Additionally, it is noticeable from Fig. 2c that the column coupling method (method-A+B) requires longer separation time to resolve all target components (11 components with almost 17 min of separation time) than both single methods (either method-A or method-B). Method-A requires less than nine min to resolve six components in the test mixture (Fig. 2a), while the five components in test mixture were resolved using method-B with less than 11 min of separation time (Fig. 2b). Regardless the separation time required for resolving the all those 11 target components, the column coupling (method-A+B) was found to be more efficient than both single column method (method-A and method-B) in term of its ability to accommodate the need to identify the arget components in the test mixture from one sample injection. Otherwise, other additional works are needed when the single column method is used such as column replacement. Besides, development of each method (method-A or method-B) to fit to its analytical purpose is also demanded. In a word, the drawbacks of the single column method (method-A or method-B) can be compensated by using the column coupling method (method-A+B). Other published experiments [20, 21] have also reported the advantageous of the coupling method of the GC techniques. Furthermore, Fig. 2c show that both columns have independent components retention. There were no component intended to elute from one column that was seen to co-elute in the other column. Therefore, it can be concluded that the column coupling method in

this study has fulfilled the principle of orthogonality [14].

Moreover, it is also observed from the Fig. 2a that the CH_4 (component 10) as a hydrocarbon component in the test mixture could not be resolved in the SP-700 column. In principle, the CH_4 could be resolved on SP-1700 column, but the ability of the SP-1700 column (method #1) is limited by the operating condition of the GC-TCD under this study such as oven temperature used and starting time of the separation of the target component. Based on the SP-1700 column specification [17], the CH_4 and air are resolved before the C_2H_6 (component 1). Nevertheless, from Fig. 2a, it can be observed that the C_2H_6 (component 1) was resolved at t_R = 2.68 min, meaning that the CH_4 and air (in the form of N_2+O_2 composite) cannot be resolved on SP-1700 before the C_2H_6 (component 1) under experimental condition of this study. On the other hand, both CH_4 and air were then resolved on MS-5A column (column #2) followed by the detection using TCD (Fig. 2b). In MS-5A column (Fig. 2b), the air was resolved as its individual component i.e., O_2 (component 8) and N_2 (component 9).

In general, however, all aforementioned finding indicates that the development of the GC measurement method can be, sometime, tricky and requires technical experience.

Effect Column Temperature and Carrier Gas flow rate

The effect of column temperature and the flow rate of carrier gas was solely intended to examine the ability of the operating condition of the GC-TCD to influence the measurement results in term of a possible change in the retention time (t_R) of the target component.

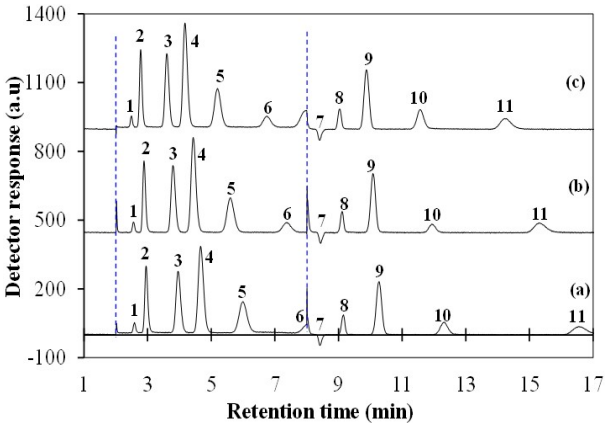


Figure 3. Chromatogram profile of the 11 target components separated using column coupling method (method-A+B) under different column temperature: a). 35°C, b). 40°C, and c). 45°C. The vertical blue dotted line indicates the time position of the switching valve.

Figure 3a-c presents a chromatogram profile of the target components in the test mixture using the GC-TCD under different column temperature. It can be clearly observed from Fig. 3a-c that changes in the column temperature led to change in the retention time (t_R) of the target components. The details of the evaluated data are tabulated in Table 3, showing that increasing of the column temperatures decrease the t_R of the target

component. In addition, Fig. 4 shows a representative example concerning the dependency of the t_R of target components on the column temperature. It is observed from the Fig. 4 that the t_R of the target compound linearity (R^2 = 0.9789 – 1.0000) decreased by increasing the column temperature. This phenomenon can be ascribed as follows. At lower column temperature, the target components spend most of its time (condensed) in stationary. Under this condition, a longer time is needed for the target component to move freely into mobile phase and push along the column to the detector. For other component that is not included in Fig. 4, the linearity coefficient (R^2) of the decreasing retention time due to the column temperature variation effect can also be seen on Table 3.

Table 3. Retention time of the target components at different column temperature.

Target comp.	Comp. No.	Colum temperature (°C)			R^2
		35	40	45	
C_2H_6	1	2.59	2.54	2.50	0.9789
CO_2	2	2.96	2.88	2.79	0.9957
C_3H_8	3	3.97	3.78	3.61	0.9967
C_3H_6	4	4.68	4.42	4.18	0.9968
Iso-C_4H_{10}	5	6.00	5.59	5.21	0.9979
n-C_4H_{10}	6	-	7.37	6.60	-
H_2	7	8.43	8.39	8.35	1.0000
O_2	8	9.16	9.10	9.04	0.9947
N_2	9	10.28	10.07	9.88	0.9982
CH_4	10	12.34	11.94	11.58	0.9995
CO	11	16.58	15.30	14.25	0.9958

Conversely, at higher column temperature, the equilibrium occurs to opposite direction where the target components spend most of its time in mobile phase (non-condensed in stationary phase). Since then, the shorter time is needed by the target component to move freely along the column to detector [22]. The findings indicate that the column temperature is highly affecting the GC retention time of the target component. In a word, the higher column temperature would decrease the t_R of the target component and vice versa [23, 24].

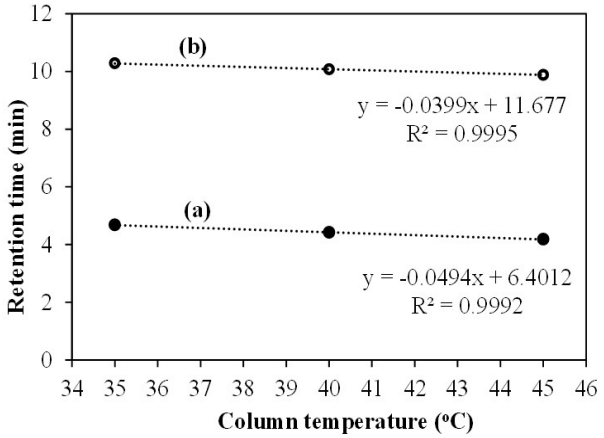


Figure 4. Retention time dependency of: a). C_3H_6, and b). N_2 on the column temperature of the GC-TCD.

Moreover, Fig. 5a-c depicts a chromatogram profile of the target component measured at different flow rate of carrier gas. From Fig. 5a-c, it can be roughly evaluated that change in the flow rate of carrier gas has influenced the t_R of the target components significantly. In detail, Table 4 lists the obtained data regarding the effect of carrier gas on the t_R of the target components. From

Table 4, it was found that increase of the flow rate of carrier gas decreases the t_R of the target components. A representative graphical example is depicted in Fig. 7, indicating the linearity decreases of the t_R of the target components (R^2 = 0.8069 – 0.9999) by increasing the flow rate of the carrier gas. Since the flow rate determines the rate of carrier gas to carry target components passing through the column, therefore, a longer t_R can be achieved at a lower flow rate of carrier gas and vice versa [25]. This phenomenon indicates that faster flow rate of the carrier gas lead to decrease not only the velocities of vaporized molecules spent in the column (stationary phase), but also the time spent in the mobile phase [26]. The findings are indicated that adjustment the flow rate of carrier can be used as an important technique for achieving a desired t_R in a GC measurement in practice. For other component that is not included in Fig. 7, the linearity coefficient (R^2) of the decreasing retention time due to the carrier gas flow rate variation effect can also be seen on Table 4.

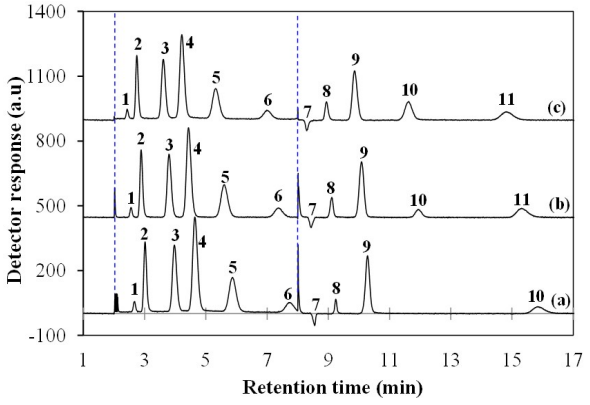


Figure 5. Chromatogram profile of the 11 target components separated using column coupling method under different flow rate of carrier gas: a). 25 ml/min, b). 28 ml/min, and c). 31 ml/min. The vertical blue dotted line indicates the time position of the switching valve.

In addition, effect of the flow rates were observed by plotting different flow rates versus their corresponding height equivalent theoretical plate (HETP) in a graph. This graph, illustrated in Fig. 6, can be utilized to define the optimal flow rate using Van Deemter equation. According to Van Deemter theory, the flow rate can be considered optimal when the corresponding HETP is at minimum [27], which is 25 ml/min as shown in Fig.6. However, Van Deemter equation cannot always be applied in coupling column method. As seen in Fig.5a, setting the carrier gas flow rate at 25 ml/min resulted in an interference to the peak of n-C_4H_{10} caused by the valve switching. This issue can be solved by delaying the valve switching time, but at the cost of longer and less efficient analysis run time. This factor should be taken into consideration when selecting carrier gas flow rate in column coupling method, beside the Van Deemter equation. For example, it can be seen in the chromatogram shown by Fig. 5b that at higher flowrate, 28 ml/min in this case, a good separation between component peaks can be achieved without sacrificing a peak or prolonging the analysis run time.

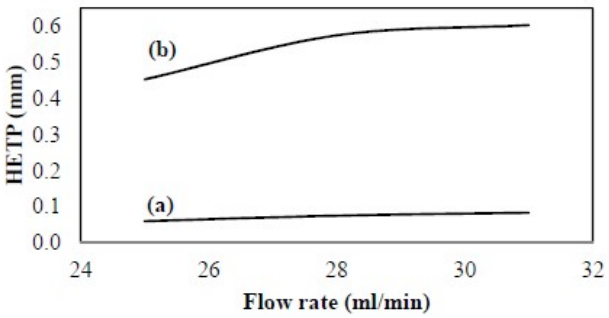


Figure 6. Effect of flow rate of carrier gas on the HETP between: a). C_3H_8 and C_3H_6, and b). O_2 and N_2.

Application of Column Coupling Method

For the qualitative application of the column coupling method (method-A+B), two commercial natural gas samples containing unknown components were measured. The qualitative analysis relies on comparing the retention times of the peaks in an unknown sample with those of known standard and the results are presented in Fig. 8b-c. The chromatogram of the test mixture was only included for a comparison purpose (Fig. 8a).

Table 4. Retention time of the target components at different carrier gas flow rate.

Target comp.	Comp. No.	Carrier gas flow rate (ml/min)			R^2
		25	28	31	
C_2H_6	1	2.68	2.54	2.42	0.9965
CO_2	2	3.02	2.88	2.74	0.9993
C_3H_8	3	3.98	3.78	3.60	0.9992
C_3H_6	4	4.65	4.42	4.21	0.9993
Iso-C_4H_{10}	5	5.88	5.59	5.31	0.9988
n-C_4H_{10}	6	7.75	7.37	6.99	0.9998
H_2	7	8.56	8.43	8.29	0.9998
O_2	8	9.25	9.10	8.93	0.9988
N_2	9	10.29	10.07	9.85	0.9999
CH_4	10	15.86	11.94	11.62	0.8069
CO	11	-	15.30	14.80	

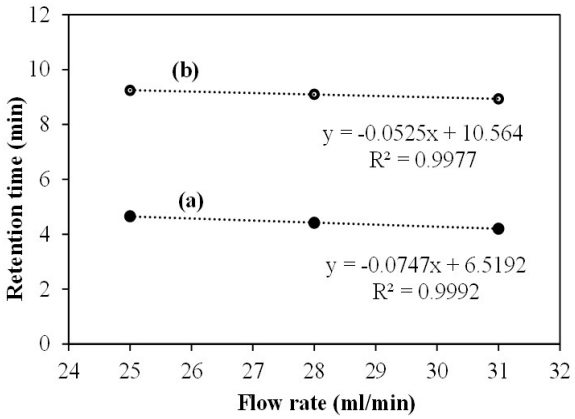


Figure 7. Effect of flow rate of carrier gas on the t_R of: a). C_3H_6, and b). N_2.

From Fig. 8b-c, it can be seen that some unknown components were identified qualitatively. From Fig. 8b (Sample-1), seven components were identified including 1, 3, 5, 6, 8, 9, and component 10. Moreover, Fig. 8c presents a chromatogram profile of sample-2, indicating that sample-2 contains six components including component 1, 3, 5, 6, 8, and component 9. Nevertheless, other component at low concentration may exist in those two natural gas samples, but their present can not be identified using the method used under this study.

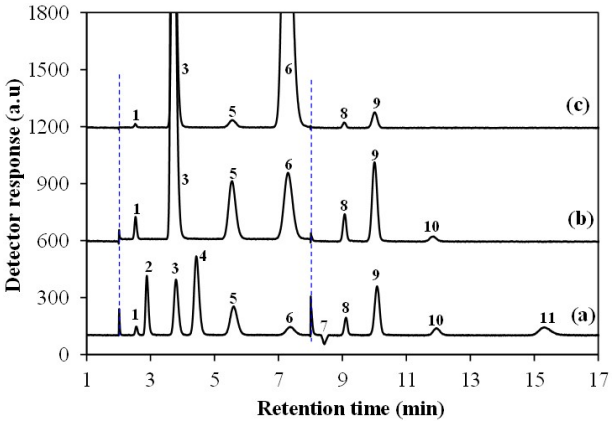


Figure 8. Representative of the GC-TCD chromatogram of the gas sample obtained using column coupling method: (a) test mixture, (b) sample-1, and (c) sample-2. The vertical blue dotted line indicates the time position of the switching valve.

Conclusions

In conclusion, an efficient column coupling method has been evaluated for a qualitative simultaneous identification of some permanent and hydrocarbon gases in test mixture. The evaluated column coupling method (method-A+B) is more benefit than single column methods (either method A or method B). The t_R of the target componenet is highly influenced by column temperature and flow rate of carrier gas. Application of the column coupling method for identification of the target components in natural gas samples implies that the method can be used in a routine work. Since this evaluation study is only subjected to a qualitative identification; thus, further development of the column coupling method for quantitative measurement purpose is still promising to be carried out.

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